Anthropogenic and impact spherules: Morphological similarity and chemical distinction – A case study from India and its implications

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This paper provides first report of silica-rich anthropogenic spherules of varying colour, shape, size, surface texture and chemical composition found in road-deposited sediments (RDS) of Allahabad city, Uttar Pradesh, India. Morphological details and lithophile elemental composition of the silica-rich spherules are compared to microtektites and impact spherules from India to demonstrate their striking morphological similarities and chemical variability. This study suggests the need to use spherule data carefully while assigning an impact origin to spherule-finds or spherule-bearing lithological horizons.

1. Introduction

The evidences of oldest impact event on Earth due to the collision of large extraterrestrial objects come from Archean spherule layers exposed in South Africa and Australia (∼3.5–2.5 Ga; Glikson 2005; Simonson *et al* 2009 and references therein). The recent report about the catastrophic spread of coal fly ash spherules along with other particulate matter from the Lake Buchanan section, Sverdrup Basin, Canadian High Arctic (Grasby *et al* 2011) is believed to be related to/associated with the latest Permian extinction (LPE). However, spherules are formed in several ways in nature (Simonson *et al* 2009; French and Koeberl 2010; Saragnese *et al* 2010; Weiss *et al* 2010; Yang *et al* 2010). They can be of terrestrial (biogenic, industrial, diagenetic and volcanic), extraterrestrial (Fredriksson 1956) and they may also form due to the impacts of crater-producing meteorites (Raukas 2000; Osawa *et al* 2003; Kofman *et al* 2010). Early work on cosmic spherules was done by Fredriksson (1956) and it was shown that spherules as ablation products of meteorites as they pass through the Earth's atmosphere leading to the melting of interplanetary dust particles in the upper atmosphere as they get heated above their liquidus due to atmospheric friction. The anthropogenic source of spherules can be varied. This includes the combustion of fossil fuel (e.g., in diesel engines) contributes to the formation of spherules and their aggregates (Kim *et al* 2009). In addition, anthropogenic spherules can also originate from industrial and/or domestic heating systems (Goddu *et al* 2004; Gautam *et al* 2005). Coal combustion due to volcanic activity, thermal power plants and steam generation units

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gives rise to significant emission of particulate matter and pollutants (Dayal and Sinha 2005; Sharma *et al* 2005; Bhanarkar *et al* 2008; Grasby *et al* 2011; http://elements.geoscienceworld.org/content/vol6/issue4/#ARTICLES). Unless evidence for meteorite impact is demonstrated, it is nearly impossible to differentiate between anthropogenic spherules, microtektites and impact spherules based on their morphology and/or geochemistry alone (Marini 2003; Buchner *et al* 2009; French and Koeberl 2010). However, the detection of shock metamorphic effects in mineral grains such as quartz or zircon as constituents of spherule layers provides unequivocal evidence for impact, as in the case of the K/Pg boundary layer related to the ∼66 Ma Chicxulub impact on the Yucatán peninsula, Mexico (e.g., Bohor 1990; Schulte *et al* 2010), the distal ejecta layer in the United Kingdom derived from the ∼215 Ma Manicouagan impact structure, Québec, Canada (Walkden *et al* 2002) or worldwide-distributed Upper Eocene impact ejecta in connection with the ∼35 Ma Popigai impact in Siberia (Montanari and Koeberl 2000; Whitehead *et al* 2000). Nevertheless, some putative impact ejecta layers still lack convincing evidence of shock metamorphic features, such as the spherules of the Barberton Greenstone Belt in South Africa earlier attributed to impact (Hofmann *et al* 2006).

As a result, in some instances anthropogenic spherules have been misidentified as microtektites (Marini 2003). At times magnetic properties of spherules have been used to decipher their extraterrestrial origin, whereas many consider them as contaminated terrestrial objects (Buchner *et al* 2009). A large database exists on the morphology and geochemistry of impact-generated spherules including tektites but similar data on anthropogenic spherules is semi-quantitative and scarce (Blaha *et al* 2008). In India, microtektites have been reported from the Indian Ocean sea floor based on their morphology (Prasad and Sudhakar 1998; Pattan *et al* 2010) and recently a study has been undertaken on the impact spherules from the basalt-hosted Lonar structure, India (Misra *et al* 2009) to understand the projectile chemistry. In case of Ramgarh structure, the morphological similarity and chemistry of 'spherules' have also been cited as impact diagnostic criteria (Sisodia *et al* 2006) although this

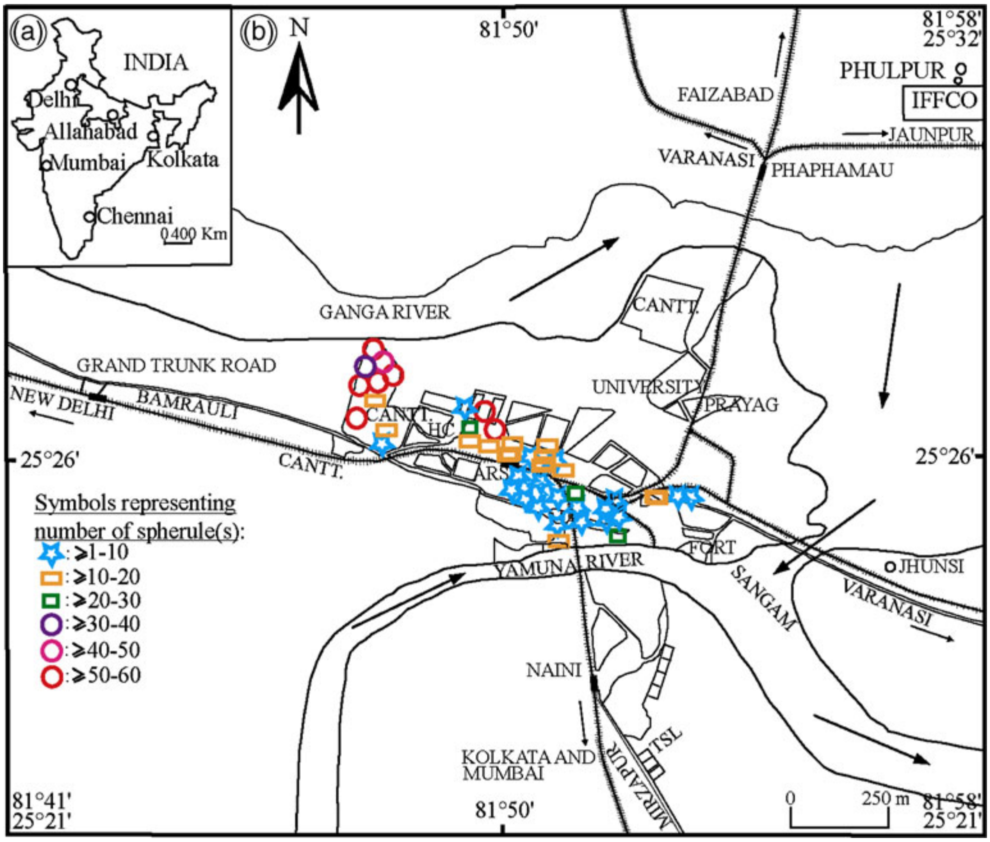

Figure 1. (**a**) The inset map of India showing the state of Uttar Pradesh and Allahabad city. (**b**) The traffic network map of Allahabad city with sample locations and number of spherules recovered per location shown with different symbols: Allahabad Railway Station (ARS), Cantonment (CANTT), High Court (HC).

claim has been refuted later (Reimold *et al* 2006). However, the spherical shape of spherules is neither an indicator of impact cratering nor of melting (French and Koeberl 2010).

The present study provided the first report of silica-rich spherules (SS) from road-deposited sediments (RDS; after Thorpe and Harrison 2008) of Allahabad city, U.P., India (figure 1) of anthropogenic origin having excellent morphological similarity with impact-related spherules and microtektites known from the Indian subcontinent. This work also reports the chemical composition of anthropogenic glass spherules from Allahabad area for the first time and compares them with published data on microtektites from the Indian Ocean sea floor and spherules from the Lonar structure to establish their respective similarity and differences in terms of morphology, size, shape, colour and chemistry. This is intented to carefully evaluate the growing number of reports of probable/possible impact craters, microtektites and impact spherules from the Indian subcontinent mainly based on spherule morphology and chemistry.

2. Materials and methodology

The present study is focused on spherules observed in the RDS of Allahabad city. The road dust samples (200 gm each) were collected from 150 locations in plastic bottles during the months of April and May, 2009 covering the Allahabad city limits (25°27′33.40″–25°26′33.40″N and 81°52′45.47″–81°52′33.40″E) and parts of the two satellite industrial townships, viz., Naini and Phulpur (figure 1) covering nearly 150 km^2 area. Only 50 samples were included in the present study. Ten samples of SS were selected from different locations for analyses of lithophile elements by Electron Probe Micro-Analyser (Cameca SX-100) at the Physical Research Laboratory, Ahmedabad. The spherules were mounted with Araldite® on a conducting metallic stub of 2.5 cm diameter and coated with either gold or carbon. The electron microprobe analyses of spherules were performed on polished thin sections. The analyses were carried out at 10–15 kV accelerating voltage, 25 mA beam current and 1–10 μm beam diameter. Both natural and synthetic standards were used for calibration. The detection limit was between 0.1 and 0.5 wt% depending on the element. SEM and BSE (Backscattered Electron) images were acquired to observe surface texture and chemical zonation, respectively. For every spherule at least five analyses were made at different spots. The number of spherules obtained from the representative samples of RDS range from 1 to 60 with an average of 18 spherules per location showing the spatial variability in their number (figure 1). The RDS collected from different locations across Allahabad city, in general, contain/comprise angular to sub-rounded clasts of quartz and feldspar, flakes of mica, gypsum flakes, lumps of cow dung, bones, broken glass, sugar cane husks, seeds, plastic and metallic fragments and spherules (both metallic and silica-rich). The spherules are glassy in nature, which has been verified on the basis of standard petrographic techniques and X-ray diffraction study. This study is primarily confined to characterize the SS in the RDS identified in meso- to microscopic scale observations. About 10 gm of samples were air-dried and used for microscopic observation and separation of different constituents. The samples were divided into two grain size fractions using a 35 mesh/500 μm sieve (ASTM; American Society for Testing Materials). Spherules were handpicked under a Leica stereozoom microscope. The abundance of spherules is less than 1 vol% of RDS samples. The locations of 50 samples, number of spherules observed in each sample and morphology and colour of spherules are summarized in table 1.

3. Shapes and surface features of the spherules

The specific properties of spherule shape have been used as an important criterion to identify spherules of impact origin (Simonson 2003) and shapes of impact spherules may vary from more angular to typically spherical types (Simonson *et al* 2000). Although spherical shapes of melt particles are the most common (aerodynamically-shaped) type observed, certain spherule shapes (teardrops and dumbbells) can be very common to a particular impact structure (e.g., Chicxulub, Mexico; Smit *et al* 1992). Sometimes the nonspherical shapes (ovoid, elongated, teardrop and dumbbell) are considered to have developed due to the breakup and spin of melt droplets as they get transformed from melt to glass (Simonson 2003). Agglutinated shapes have formed due to collision of molten spherules in flight but the exact processes giving rise to various external shapes of spherules is not fully answered (Simonson 2003). The microtektites reported from Indian Ocean are mostly spherical, however dumbbell shapes are also observed (Prasad and Sudhakar 1996) and ‘impact spherules’ from Lonar structure include shapes like spheres, teardrop, cylinders, dumbbells and spindles (Misra *et al* 2009). In addition, cratered and pitted surfaces of microtektites have been attributed to their impact origin (Prasad and Sudhakar 1996; Margolis *et al* 1971).

Table 1. *Location details of 50 samples, number of spherules per 10 gm of sample and morphology and colour of spherules based on meso- and microscopic studies. Traffic implies vehicular traffic. Colourless spherules are transparent.*

Sl. no.	Sample location (Lat.; Long.)	Description of sampling location	No. of spherules	Morphology	Colour
1.	Anglo Bengali College, Civil Lines (25°27′00.58″N; 81°50′24.66″E)	Commercial area; low traffic	17	Spherical to oval	Colourless, grey, white, reddish black
2.	Purvanchal Vidhut Vitran Nigam Limited, Civil Lines (25°26′48.22″N; 81°50′20.82″E)	Commercial area; heavy traffic	5	Spherical to oval	Colourless, grey
3.	Beneath Railway dat ka pool, near Niranjan Talkies (25°26′39.19″N; 81°50′16.77″E)	Commercial area; heavy traffic	7	Spherical to oval	Colourless, grey, reddish yellow
4.	Ghantaghar Intersection, Chowk (25°26′26.33″N; 81°50′06.45″E)	Densely populated residential and commercial area; heavy traffic	3	Spherical	Colourless
5.	Church, Chowk (25°26′19.45″N; 81°50′02.13″E)	Commercial area; heavy traffic	5	Spherical to oval	Grey, purple
6.	Atul Chair Houses, Chowk (25°26′15.17″N; 81°50′03.61″E)	Commercial area; moderate traffic	5	Spherical	Grey
7.	Kotwali Bahadurganj (25°26′13.43″N; 81°50′02.02″E)	Commercial area; moderate traffic	5	Spherical to oval	Colourless, white, light yellow
8.	Chandralok Chauraha (near Rajarshi Mandapam), Mutthiganj (25°26′13.23″N; 81°50′04.33″E)	Commercial and residential area; heavy traffic	25	Spherical to oval	Grey, brown, white
9.	Batasha Mandi, Chowk (25°26′14.45″N; 81°50′02.13″E)	Commercial area; heavy traffic	1	Oval	Light yellow
10.	Rambagh, dot pool, Eid-Gaah (25°26′19.35″N; 81°50′10.37″E)	Commercial area, auto-rickshaw stand; heavy traffic	10	Spherical	Grey, brown, white, light yellow, colourless
11.	Kidgang, dat ka pool (25°26′08.56″N; 81°50′42.38″E)	Commercial area; heavy traffic	2	Spherical	Grey
12.	Arya Kanya Degree College, Mutthiganj (25°25′54.55″N; 81°50′40.13″E)	Densely populated residential and commercial area	3	Spherical	Purplish black, grey
13.	Kajal Cinema, Kidganj (25°26′06.23″N 81°50′54.74″E)	Commercial area; moderate traffic load	5	Spherical	Grey, colourless, brown, white
14.	Rani Watika, Krishna Nagar, Kidganj (25°26′04.34″N; 81°50′58.22″E)	Residential and commercial area	8	Spherical	Grey
15.	Allahabad Degree College, Kidganj (25°26′02.12″N; 81°50′59.11″E)	Commercial area; heavy traffic	15	Spherical, oval and dumbbell	Colourless
16.	Pawansut Hanuman Mandir (near High Court) (25°27′04.28″N; 81°41′17.56″E)	Commercial area; heavy traffic	22	Spherical and elongated	Colourless, grey, white
17.	Petrol Pump (near High Court) (25°27′04.49″N; 81°41′18.69″E)	Commercial area; heavy traffic	10	Spherical with pits and cracks	Colourless, grey

18.	Church, Pathar Girja, Civil Lines (25°27′03.93″N; 81°48′17.38″E)	Commercial area; low traffic	60	Spherical, oval and fused type	Colourless
19.	Axis Bank, Vinayak Tower, Civil Lines (25°26′01.35″N; 81°50′03.96″E)	Commercial area with little greenery	16	Spherical, oval and dumbbell	Colourless, grey
20.	Government Girls Inter College Chauraha, Civil Lines (25°27′03.50″N; 81°49′43.64″E)	College area; low traffic	59	Spherical, oval and fused type	Colourless, grey, white
21.	Bank of Baroda, Civil Lines (25°25′03.28″N; 81°51′19.47″E)	Commercial area; moderate traffic	13	Spherical	Colourless, grey
22.	Subash Chandra Bose Chauraha, Civil Lines (25°25′04.58″N; 81°51′34.46″E)	Residential and commercial area; heavy traffic	15	Spherical and fused type	Colourless
23.	Indira Bhawan Gate, Civil Lines (25°27′03.12″N; 81°51′17.34″E)	Commercial area; heavy traffic	16	Spherical	Colourless, grey
24.	Atul Chair Houses, Chowk (25°26′15.17″N; 81°50′03.61″E)	Commercial area; heavy traffic	2	Distorted oval	Colourless
25.	Shiv Charan Lal Road Chauraha, Bahadurganj (25°26′13.24″N; 81°50′03.11″E)	Commercial area; moderate traffic	2	Spherical	Grey, white
26.	Zero Road (Chandralok Talkies) (25°26′13.45″N; 81°50′8.13″E)	Heavy traffic load, residential area and commercial area	7	Spherical	Colourless, grey, silver grey
27.	Ram Krishna Sewashram, Mutthiganj (25°25′53.45″N; 81°50′38.34″E)	Densley populated residential area; heavy traffic	5	Spherical and fused	Colourless, grey
28.	E.C.C. Gate (Gaughat) (25°26′43.34″N; 81°50′44.06″E)	Residential and college area	13	Spherical to oval	Colourless, grey
29.	K.L. Katju Chauraha, Kidganj (25°26′05.41″N; 81°50′57.77″E)	Commercial area; moderate traffic	7	Spherical, hemi-spherical and fused type	Colourless, grey, white, brown, light yellow
30.	Tulsiani Plaza, Civil Lines (25°27′03.28″N; 81°51′7.44″E)	Commercial area; low traffic	16	Spherical, oval and fused type	Colourless, grey
31.	Big Bazaar, Civil Lines (25°27′00.66″N; 81°50′10.77″E)	Commercial area; heavy traffic	7	Spherical to hollow spherical	Colourless, white
32.	Tulsi Chauraha (near Hanuman Mandir), Civil Lines (25°26′58.59″N; 81°50′23.44″E)	Heavy traffic with little greenery	13	Spherical to oval	Colourless, grey
33.	Superintendant Chandra Shekhar Park, Civil Lines (25°26′56.57″N; 81°50′41.23″E)	Lush green area; low traffic	14	Spherical, elongated and fused type	Colourless, grey
34.	C.A.V. Inter College, Civil Lines (25°26′51.79″N; 81°50′57.31″E)	College area; low traffic	11	Spherical	Colourless, grey, white, brown

Table 1. *(Continued.)*

Sl. no.	Sample location (Lat.; Long.)	Description of sampling location	No. of spherules	Morphology	Colour
35.	C.A.V. Inter College, Civil Lines (25°26′51.79″N; 81°50′57.31″E)	College area; low traffic	3	Spherical to hemispherical	Colourless, grey
36.	Alopibagh Tiraha, Alopibagh (25°26′38.88″N; 81°52′09.72″E)	Densly populated area; heavy traffic	4	Spherical to oval	Colourless, grey
37.	New Cantonment (25°26′55.42″N; 81°48′54.41″E)	Residential area and green belt zone; low traffic	60	Spherical, oval and fused type	Colourless, pale yellow
38.	New Cantonment (25°27′04.81″N; 81°48′54.54″E)	Residential area and green belt zone; low traffic	40	Spherical, oval and fused type	Colourless
39.	New Cantonment (25°27′18.74″N; 81°48′57.11″E)	Residential area and green belt zone; low traffic	48	Spherical, oval and fused type	Colourless
40.	New Cantonment (25°27′19.68″N; 81°48′58.54″E)	Residential area and green belt zone; low traffic	60	Spherical, oval and fused type	Colourless
41.	New Cantonment (25°27′25.94″N; 81°48′59.43″E)	Residential area and green belt zone; low traffic	60	Spherical, oval and fused type	Colourless
42.	46, Cannon Officers Mess, New Cantonment (25°27′49.04″N; 81°49′00.03″E)	Residential area and green belt zone; low traffic	60	Spherical, oval and fused type	Colourless
43.	Ashwani Dronacharya, New Cantonment (25°28′02.48″N; 81°48′38.29″E)	Residential area and green belt zone; low traffic	10	Spherical, oval and fused type	Colourless
44.	Ashwani Dronacharya, New Cantonment (25°28′02.69″N; 81°48′38.58″E)	Residential area and green belt zone; low traffic	13	Spherical and fused type	Colourless
45.	Ashwani Dronacharya, New Cantonment (25°28′00.48″N; 81°48′37.16″E)	Residential area and green belt zone; low traffic	8	Spherical and hemispherical	Colourless
46.	Alop Shankari Mandir, Alopibagh (25°26′36.64″N; 81°52′12.24″E)	Residential area and green belt zone; low traffic	3	Spherical	Colourless
47.	District Education Training Centre, Civil Lines (25°26′58.67″N; 81°50′23.24″E)	Little greenery; heavy traffic	20	Spherical	Colourless
48.	Trikonia, Sabji Mandi, Madhwapur (25°26′34.33″N; 81°51′46.15″E)	Densely populated area; heavy traffic	3	Spherical and teardrop	Colourless
49.	Tulsi Chauraha (near Hanuman Mandir), Civil Lines (25°26′58.57″N; 81°50′3.54″E)	Little greenery; heavy traffic	12	Spherical to oval	Colourless
50.	New Cantonment area (25°27′35.64″N; 81°48′54.11″E)	Residential area and green belt zone; low traffic	60	Spherical, oval and fused	Colourless

4. Spherule sizes and their spatial distribution

The size range of most Archean to Palaeoproterozoic impact spherules is constrained between 60 and 2000 μm, although some can measure up to 15–20 mm across (Simonson 2003). The spherules from Lonar crater (Misra *et al* 2009) are sub-millimeter (0.3–1 mm) to centimeter-sized (up to ≈30 cm) and the microtektites from Indian Ocean range in size between 110 and 980 μm. The spherules can travel several hundreds of km suspended in air from various sources. In case of impact structures, their spatial distribution is divided into proximal and distal ejectas. Australasian tektites strewn field are known to spread over >1 million km^2 area (Glass and Wu 1993).

5. Colour variation in spherules and their occurrences

The colour of the anthropogenic spherules (present study) varies from colourless (transparent) to grey, opaque white, brown, yellow and dark grey. The presence of colourless (transparent) spherules is dominated in the city while dark grey ones are observed in the southern part, i.e., industrial area, Naini of the city. On the contrary, the impact spherules are mostly coloured (orange, greenish, amber, brownish and dark grey; Weiss *et al* 2010) and microtektites are yellowish, yellowish white, white, greenish yellow and green in colour (Pattan *et al* 2010). The anthropogenic spherules are generally colourless as their silica content is very high and near absence of transition metal elements.

6. Chemistry of the spherules

In the absence of diagnostic evidence, the origin of spherules has always been a matter of debate. However, the geochemical analysis of spherules and/or spherule layers in a number of cases (based on PGEs abundances and relevant isotopic concentrations) has helped to resolve the problem pertaining to their origin (Lowe *et al* 1989; Kyte *et al* 2003; Simonson *et al* 2009). Since the projectile composition is not always chondritic, PGEs concentration too has limitations. Similarly microtektites also show wide chemical variation (basaltic to nearly pure silica in composition). The composition of anthropogenic spherules also depends on the chemistry of raw material(s) and at times practically impossible to distinguish them from spherules of impact origin. The nature of particulate pollutants can be predicted from the study of fly ash from the coal-based industrial heating systems (Jordanova *et al* 2006). The particles mainly comprise elements like, Si, Al, S, Ca, and Fe since raw coal is known to constitute kaolinite, quartz, siderite, calcite, pyrite, gypsum and sulphur (Xie *et al* 2009 and references therein). Many features, characteristic of Indian fly ash, are considerably different from the corresponding features of fly ash generated elsewhere (Sarkara *et al* 2005). However, there is currently no comprehensive dataset on the systematic geochemistry of anthropogenic spherules in the literature.

7. Results and discussion

The present study is based on the detailed analysis of 167 spherules from 50 representative sample sites. The shapes of the silica spherules from Allahabad RDS are mostly spherical to ovoid. The specific shapes observed include elliptical, dumbbell, cylindrical, tear-drop and spindle (figure 2a–e). Nearly 84% of the spherules are spherical and 16% of the spherules show the agglutinated form (adherence and coalescence features). Most or all of these aggregates tends to have appeared from the crystallization of the original melts (e.g., Scally and Simonson 2005; Sweeney and Simonson 2008) (figure 2f). The surface textures of anthropogenic spherules generally vary from smooth to pitted types having majority of irregular pits with some circular and jagged ones showing their resemblance to that of impact spherules. About 10–50% of the surface area of the bigger (200–1000 μm) spherules show pitted appearance ('cratered surface') whereas the smaller ones are relatively smooth (figure 2g, h). However, ring-like features reported by Prasad and Sudhakar (1998) around the pits in Indian Ocean microtektites have not been observed in silica spherules from the Allahabad RDS. The presence of bubbles and multiple bubble trails inside SS is occasionally noted.

The spherules present in Allahabad RDS measure from 100 to 200 μm in size (in the case of 35 mesh-sized sieved dusts). However, in the unsieved samples, the size varies between >200 and 1000 μm. The spherules in the size range of 100–200 μm are predominantly present in the vicinity of main industrial area (Naini; figure 1) and are mainly grey to dark grey in colour whereas the colourless spherules (>200 up to 1000 μm) can be seen both in residential and industrial areas of the city (figure 2a, b). The anthropogenic spherules observed in different parts of the Allahabad city exhibit a size range between 0.55 and 1.67 mm (figure 3). The size of the spherules shows a polymodal distribution with maximum number of spherules lying between 0.8 and 1 mm and their size range is similar to impact spherules (table 2). The silicate glass spherules are most abundant in

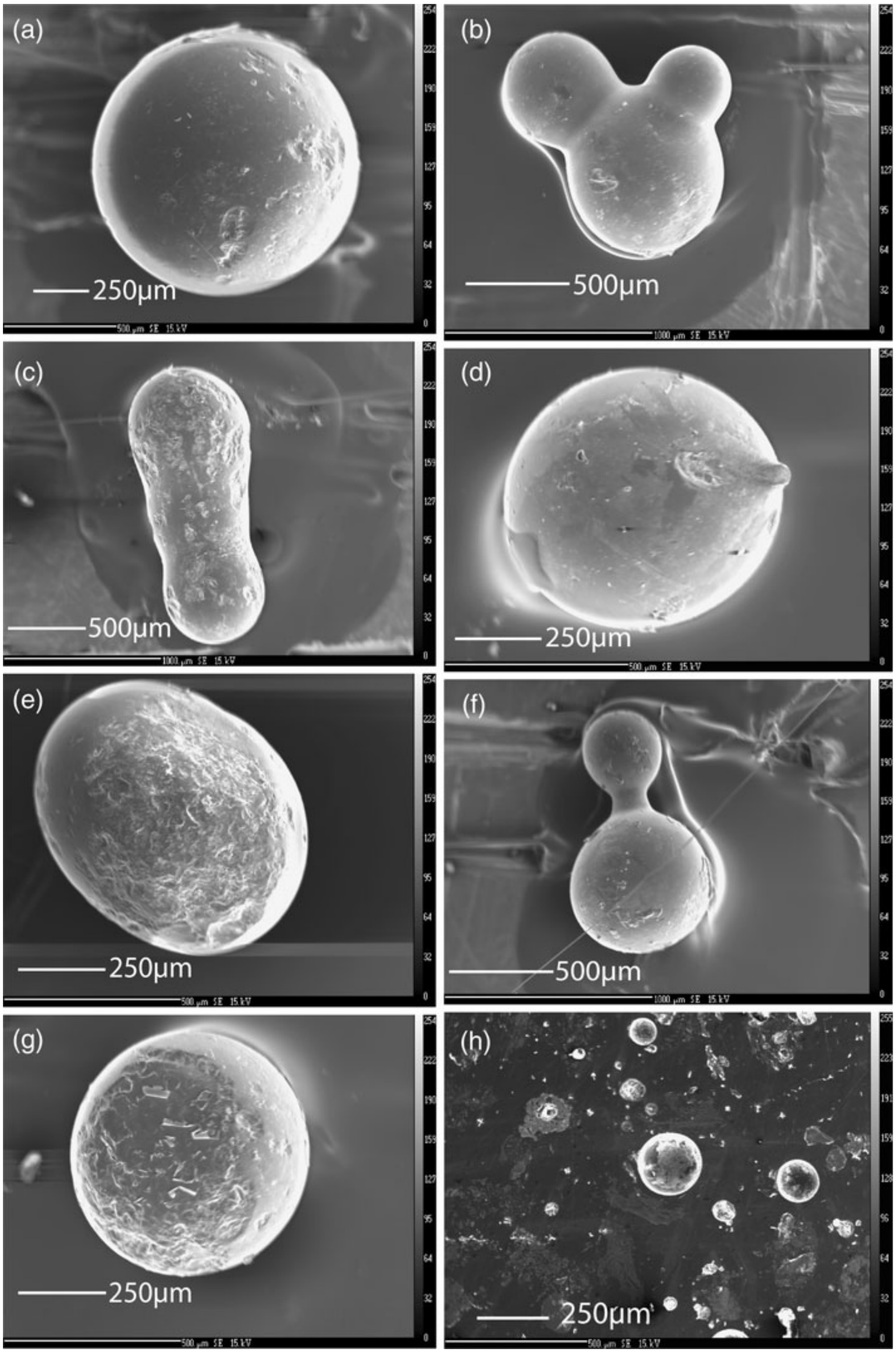

Figure 2. SEM images showing different shapes of spherules from Allahabad RDS and of fly-ash sample. (**a**) Spherical spherule with smooth surface and a few micropits. (**b**) Fused-type spherule showing two sub-spherules attached to the main one. (**c**) Elongated spherule with many micropits. (**d**) Teardrop spherule. (**e**) Oval spherule with numerous micropits. (**f**) Dumbbell spherule with a narrow neck. (**g**) Spherical spherule showing numerous micropits. (**h**) Fly ash sample from IFFCO Plant, Phulpur, Allahabad, showing many spherules.

the northern part of the city and their number decreases towards the southern part.

The 66% of all the anthropogenic spherules observed in the unsieved dust samples from Allahabad (RDS) is colourless to pale coloured (i.e., some spherules which have been noticed are light yellow coloured). The coloured anthropogenic spherules' of various hues include light grey, cream, brown and black-coloured. The metallic and dark grey spherules of the present study are predominantly observed in the Naini industrial area, Allahabad. The colourless spherules are observed both

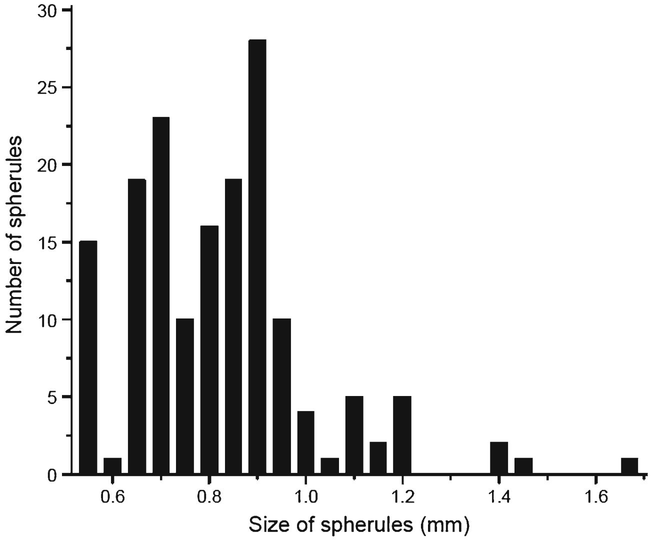

Figure 3. The size of 167 anthropogenic spherules collected from different parts of Allahabad city show a polymodal distribution with maximum numbers lying between 0.8 and 1 mm similar to impact spherules.

in residential as well as industrial areas of the city (table 1). The yellow coloured material present on the external surface of the spherule being analyzed is sulphur.

Compositional range of the SS is given in table 2. The compositional ranges of morphologically similar spherules reported from Lonar impact structure (LS), Maharashtra, India (Misra *et al* 2009) and from microtektites (MT) in surficial sediments of the Indian Ocean (Prasad *et al* 2003) are given in table 2 for comparison. The SiO_2 content of SS is between 67.96 and 85.59 wt% with an average value of 72.09 wt%. MT and LS have lower SiO_2 contents with average values of 68.59 and 48.31 wt%, respectively. SS are comparatively rich in alkali component, Na_2O (0.19–6.79 wt%) and K_2O (0.26–1.04 wt%). The total iron content of SS expressed as FeO is low (0.07–0.40). Al_2O_3 content of the SS varies between 1.21 and 3.63 wt% and is much lower than that of MT (10.63–21.12 wt%) and LS (11.76–15.23 wt%). Both NiO and Cr_2O_3 content are low in the case of SS (0.22 and 0.1 wt%, respectively). In the case of TiO_2, the values measure up to 0.07 wt%. The compositional limits of the three spherule types (SS, MT and LS) are distinct as illustrated in the binary, Al_2O_3 *vs.* SiO_2 plot (figure 4a) and ternary, SiO_2–(CaO + MgO + FeO^T)–Al_2O_3 plot (figure 4b) and implied origin. Surficial coating of yellow granules occurring at the neck of two attached spherules is analyzed to be

Table 2. *A comparison between microtektites, impact spherules and anthropogenic spherules (present study) based on their shape, size, colour and lithophile elemental composition.*

Spherule type	Shape	Size	Colour	Chemical composition
Microtektites	Spherical, elongated, teardrop, discs or dumbbell, spindle, club-shaped, bun-shaped	<1 mm	Honey coloured, light yellow, yellowish green to opaque white	SiO_2: 56.26–75.74 (Avg. 68.59) Na_2O: 0.41–1.04 (Avg. 0.66) K_2O: 0.33–2.02 (Avg. 1.00) Al_2O_3: 10.63–21.12 (Avg. 15.33) MgO: 2.38–10.62 (Avg. 4.66) CaO: 2.06–4.14 (Avg. 3.24) FeO: 3.97–9.16 (Avg. 5.42) TiO_2: 0.56–1.07 (Avg. 0.84)
Impact spherule	Spherical, teardrop, cylinder, dumbbell and spindle	≈0.3−1 mm		SiO_2: 43.33–51.39 (Avg. 48.31) Al_2O_3: 11.76–15.23 (Avg. 13.67) Na_2O: 1.23–2.38 (Avg. 1.81) MgO: 4.95–8.93 (Avg. 6.84) K_2O: 0.19–0.78 (Avg. 0.32) CaO: 8.21–10.71 (Avg. 9.24) FeO: 11.96–16.89 (Avg. 15.27) TiO_2: 1.94–2.95 (Avg. 2.32) P_2O_5: 0.02–0.16 (Avg. 0.07)
Anthropogenic spherule (present study)	Spherical, elliptical, dumbbell, spindle, teardrop and cylinder	0.55–1.67 mm	Colourless to dark grey, opaque white, brown	SiO_2: 67.10–77.07(Avg. 72.09) Al_2O_3: 1.21–3.63 (Avg. 1.70) Na_2O: 0.19–6.79 (Avg. 2.31) MgO: 3.62–0.30 (Avg. 1.97) K_2O: 0.26–1.04 (Avg. 0.50) CaO: 5.01–10.16 (Avg. 7.57) TiO_2: 0.01–0.08 (Avg. 0.03) FeO^*: 0.07–0.40 (Avg. 0.21) P_2O_5: 0.09–0.17 (Avg. 0.13)

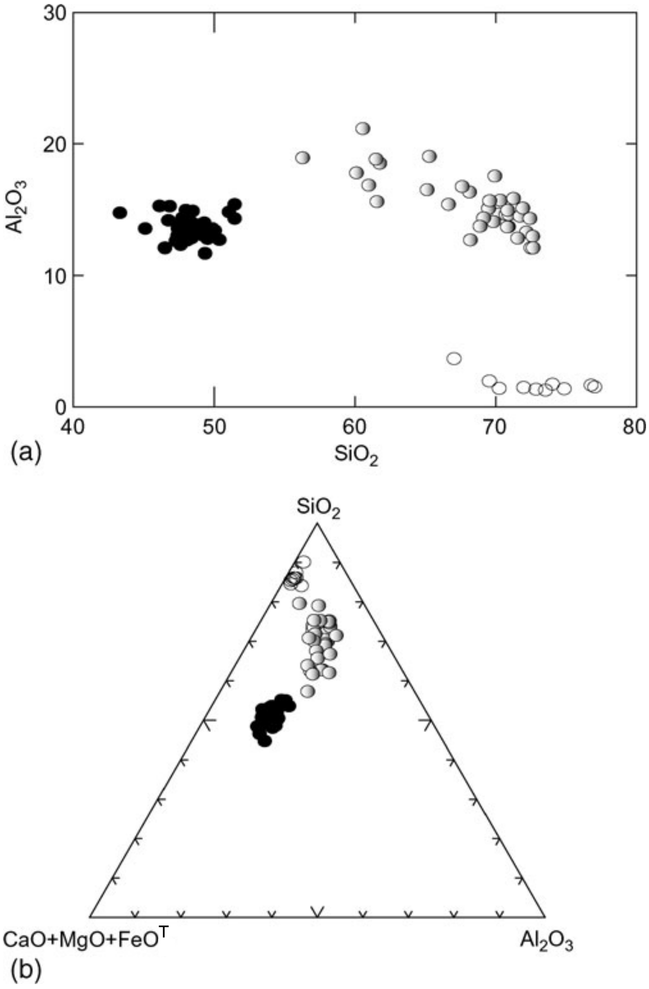

Figure 4. (**a**) Binary Al_2O_3 *vs.* SiO_2 plot showing distinct domains of SS (SS; open circle) from Allahabad RDS, microtektites (MT; shaded circle) from Indian Ocean, and spherules from Lonar impact structure, Maharashtra, India (LS; solid circle). (**b**) Ternary SiO_2–(CaO+ MgO + FeO^T)–Al_2O_3 diagram showing distinction among the three spherule types. FeO^T represents total iron expressed as FeO.

sulphur. Compositional similarity between larger spherules and the smaller ones adhering to them suggests their common origin. Presence of vesicles within SS suggests the presence of a volatile phase in the system.

The BSE-SEM images and EPMA analysis of a fly-ash sample from the steam generation of the IFFCO (Indian Farmers Fertilizer Cooperative Limited) fertilizer plant at Phulpur (25°32′10.64″N; 82°03′47.09″E), located 40 km NE of the Allahabad city shows the presence of spherules (figure 3h) and their chemistry is similar to RDS spherules of Allahabad city, respectively.

8. Conclusions

The present study suggests that the shape, size, surface features and chemistry of spherules are not diagnostic of impact cratering process and cannot distinguish microtektites and impact spherules from the coal fly-ash spherules produced from natural wildfires and thermal power plants.

The various shapes (spherical and agglutinated) of SS suggest their formation at high temperature and adherence close to their respective liquidus temperature.

The composition of SS can be defined in a SiO_2–(CaO + MgO + FeO^T)–Al_2O_3 ternary since their bulk composition in terms of the three end members lies between 80 and 90 wt%. The microtektites are slightly better defined by the three end members (96–98 wt%) compared to impact spherules (93–96 wt%).

The morphology and chemistry of fly ash spherules from the coal-based thermal power plant, Phulpur, Allahabad are identical with SS observed in RDS samples suggesting their derivation from the coal-based NTPC thermal power plant situated at Phulpur.

The spatial distribution of SS indicates their transportation to different parts of Allahabad city and its adjoining areas by wind as suspended particulate matter.

The abundance of SS is high in the northern part of the Allahabad city and their numbers per location decrease southward. However, the size of the spherules observed during the present study does not show any correlation with distance.

Hence, it is necessary to adopt a multi-pronged method to evaluate the spherules before assigning their origin as they can be carried over hundreds of km in air from various sources prior to their deposition.

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